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Using the Variable Encounter Method

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The Variable Encounter Method is applied to the study of the transient region in vibrational accommodation of cyclobutane at high temperature surfaces. Collision efficiency declines with rise of temperature. Surface collisions are more efficient than binary gas phase encounters but the wall collisions are less efficient for cyclobutane than for cyclopropane. An exponential model of transition probabilities satisfies the data.

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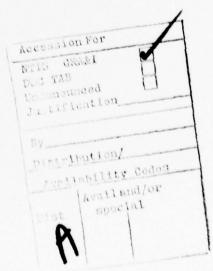S/N 0102-LF-014-6601

Transients in the Vibrational Excitation of Cyclobutane

Using the Variable Encounter Method[a]

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Abstract

The probability of reaction of cyclobutane molecules in a
fixed time interval after experiencing a known number of collisions
with a hot surface at temperatures between 749K and 1126K has been
determined using the Variable Encounter Method. Calculations util-
izing exponential or gaussian models for energy transfer enable the
average amounts of energy transferred for deactivating collisions,
$\langle \Delta E' \rangle$, to be estimated. The exponential model fits the experimental
data the best and, using this model, $\langle \Delta E' \rangle$ is 2430 cm^{-1} at 748K and
decreases to 1470 cm^{-1} at 1123K.

Introduction

A new technique (the Variable Encounter Method) has been described recently [1] for the study of the relaxation of vibrational energy of gaseous molecules on collision with a hot surface. VEM has previously been applied to the study of cyclopropane isomerization [1]. By this method, molecules are collisionally equilibrated with a cold surface of known temperature and then randomly enter a hot reactor where they experience a series of collisions with a surface (an encounter). Molecules leave the reactor at random times, usually without reaction, and are then re-equilibrated with the cold surface before re-entry into the reactor. The average number of collisions a molecule experiences with the surface of the hot reactor on each encounter can be varied by changing the dimensions of the reactor. The fraction of reaction that has occurred after a known number of encounters can be determined. This can be used to deduce information on the rates of population of vibrational states above the threshold energy for reaction, E_0, i.e., in the transient region.

In this paper we describe the application of VEM to the study of the vibrational energy relaxation in cyclobutane. This molecule decomposes to ethylene and the reaction has been well studied as a homogeneous thermal process [2-7]. The Arrhenius parameters are very similar to those for cyclopropane so that an interesting comparison with the earlier cyclopropane results is afforded.

Experimental

The reaction vessel consisted of a 2 ℓ fused quartz flask to which tubular
reactor fingers of the dimensions indicated in Fig. 1 were attached. The entrance
area of each tubular reactor was ≤ 1% of the total area of the reaction vessel.

Molecules randomly enter a reactor from the main flask. Stochastic
calculations, described in ref. 1, were used to estimate the mean number of
collisions, m , a molecule would suffer with the wall of a particular tubular
reactor before it re-emerged into the flask. The values of m were 27.2 for
reactor (i), 8.47 for reactor (ii) and 2.6 for reactor (iii) (Fig. 1). In the
case of reactor (i), molecules that collided with the walls of the antechamber
(A) but did not then enter the main part of the reactor (B) may be assumed not
to contribute to reaction. Molecules that left (B), collided with (A) and then
re-entered (B) were included in the calculation with the assumption that the
temperatures of the walls of (A) and (B) were the same.

The tubular reactors were enclosed in stainless steel furnace blocks, which
were heated by clam-shell kanthal-wound heaters. The internal diameter of the
stainless steel block was 2-3 mm greater than the outer diameter of the tubular
reactors. Reduced temperature gradients were obtained by filling the gap between
the reactor and stainless steel block with fine (∿ 100 mesh) silica sand.

The top 1 cm of reactors (i) and (ii) were heated with auxiliary heaters
made from 16 gauge kanthal wire set in alundum cement. Additional heat to the
top of the stainless steel block for reactor (iii) was supplied via 16-gauge
coils of kanthal wire set in cement in a recess in the top of the block. Maxi-
mum temperature gradients for reactors (i) and (ii) were less than ± 25°C, with
75% of the area of the reactors within ± 10°C or less. Temperature gradients
for reactor (iii) were less than ± 10°C. Temperatures were measured using
chromel/alumel and platinum/platinum-10% rhodium thermocouples cemented to the

exterior surface of the reactors. Temperatures were controlled to ± 1°C.

The reaction vessel was evacuated using a conventional glass diffusion pump to $\sim 1 \times 10^{-6}$ mm Hg, as measured by a cold cathode discharge gauge. Cyclobutane, whose major impurity was 0.2% total of propene and butene-1, was thoroughly degassed before use. Prior to kinetic runs the reactors were "aged" by pyrolysis of cyclobutane at a pressure between 3×10^{-4} and 3×10^{-3} torr for prolonged periods, at a temperature equal to the highest temperature used for that reactor. No difficulty was experienced with aging reactors (i) and (ii). Reproducible rate constants for the formation of ethene, with only trace quantities of propene and 1-butene being observed, resulted from aging for 48 hours. Aging of reactor (iii) was more difficult and required several days before reproducible rates were obtained. Propene and 1-butene formation appears to be a concurrent parallel surface-catalysed reaction, in agreement with a previous study [5]. Reactor (iii), when fully aged, gave yields of propene and 1-butene separately that amount to $\gtrsim$ 5% of ethene yields.

The reaction was studied by adding aliquots of reactant to the reaction vessel from a gas burette, pyrolysing the reactant for measured times and then rapidly freezing the reaction mixture into a trap containing a small amount of 60-80 mesh Porapak Q cooled to -196°C. Ethene product was trapped quantitatively. The relaxation time for pressure decrease during freeze down was $\sim$ 10 s. A pump-down time correction was added to the pyrolysis time used to calculate rate constants.

Analysis of the reaction products was carried out by gas chromatography using a 6 ft.-1/8" i.d. column of 28% squalane on 60-80 mesh firebrick with f.i.d. detection.

Results and Calculations

The rate of decomposition of cyclobutane to ethene was investigated over a temperature range of 749K to 1126K at an initial pressure of $\sim 1.6\times10^{-4}$ torr cyclobutane. At each temperature plots of log (fraction of cyclobutane unreacted) vs time, which were accurately linear and went through the origin, were used to determine apparent first order rate constants for decomposition. Normally, the extent of reaction at from 6-8 different reaction times was determined. A typical first order plot is shown in Fig. 2. The standard deviation of the experimental slopes of the first order plots was less than 2%. A mass balance of better than 98% was obtained.

A series of runs were carried out at 1033K in reactor (i), over the range between 9×10^{-5} torr and 5×10^{-4} torr initial cyclobutane. No change in the measured first order reaction rate constant was observed. Runs in reactor (i) in which cyclobutane and cyclopropane, at partial pressure of $\sim 2\times10^{-4}$ torr, were co-pyrolysed similarly showed no change. These mixed pyrolyses provided a very useful comparison with previous work on cyclopropane [1] and gave comparable results [8].

From a knowledge of the dimensions of the entrance orifice to each reactor, the value of m, the molecular weight of cyclobutane, and the mean temperature of the main reactor vessel, the apparent first-order rate constants were converted into mean probabilities for reaction per collision with the reactor wall, $\bar{P}_c(m)$. Values of $\bar{P}_c(m)$ are given in Table I and values of log $\bar{P}_c(m)$ vs temperature are plotted in Fig. 3.

In order to deduce information on energy transfer between cyclobutane molecules and the hot surface from the experimental data, several models for the energy transfer probability distribution function were explored. A computer simulation of the collisional processes was carried out and comparisons made between calculation and experiment.

The computer modelling procedure has been described in detail in ref. 1. Two different ("flat") models for the probability of a given down transition, $P_{\Delta E}$ were used: Model A (exponential); $P_{\Delta E} = A \exp(-\Delta E/<\Delta E>)$ for $0 \leq \Delta E \leq 9000$ cm^{-1}, $P_{\Delta E} = 0$ for $\Delta E > 9000$ cm^{-1}; Model B (Gaussian); $P_{\Delta E} = A' \exp\{-(\Delta E - \Delta E_{mp})^2/2\sigma^2\}$ for $0 \leq \Delta E \leq 9000$ cm^{-1}, $P_{\Delta E} = 0$ for $\Delta E > 9000$ cm^{-1}. Here, A and A' are normalisation constants; $<\Delta E>$, ΔE_{mp} (mp signifies most probable) and σ are parameters of the model; ΔE, ΔE_{mp} were constant ("flat") models, and σ was set equal to 0.7 ΔE_{mp}. The truncation $\Delta E < 9000$ cm^{-1} is a practical computational feature to limit the transition probability matrix to tractable dimensions. Detailed balance and completeness were maintained. It should be noted that because of truncation, the underline effective average down transition size, called $<\Delta E'>$, is not equal to $<\Delta E>$, except when the latter quantity is small; $<\Delta E'>$ may be significantly different from $<\Delta E>$ and ΔE_{mp}.

The microscopic rate constants, k_i, for decomposition of cyclobutane molecules with a specific energy content, which are required in the computer simulation, are calculated from RRKM theory. The reaction coordinate was assumed to be a C-C stretch of the cyclobutane molecule and the frequencies used for the transition state (App. A) were chosen to give agreement with the high pressure rate constant at 772K as calculated from the Arrhenius equation [3], $k_\infty = 10^{15.6} \exp(-62500/1.987T)$ sec^{-1}.

The results of the computer simulation are included in Fig. 3 for both models. In each case a value of $<\Delta E'>$ was found that produced a fit to the experimental data for reactor (iii) (m = 2.6). The curves for reactors (i) and (ii) were then calculated using the same values for $<\Delta E'>$. This approach was adopted since the value of $\overline{P}_c(m)$ for the reactor with the smallest mean collision number is the most sensitive to changes in $<\Delta E>$.

Calculations using "linear" gaussian and exponential models in which ΔE_{mp} or $<\Delta E>$ (and thus $<\Delta E'>$) were allowed to vary with initial energy according to the relationship $<\Delta E>$ (or ΔE_{mp}) $= \alpha + \beta E$, where α and β were adjustable parameters, were also carried out. These calculations gave results in poorer agreement with the experimental data for reactors (i) and (ii), particularly at the highest temperatures. The calculated values of $\bar{P}_c(m)$ for higher m are somewhat larger than those calculated for the flat models in which $<\Delta E'>$ does not vary with initial energy.

Discusssion

Conventional studies of the thermal decomposition of cyclobutane [2-7]
indicate that the reaction is a homogeneous, unimolecular reaction, although
at the lowest temperatures investigated earlier, the reaction rate did not
decline as rapidly as would have been expected for a unimolecular reaction in
the fall-off region [5,6]. This behavior was probably due to the increasing
importance of surface activation at low pressure. Indeed, surface activation
has been shown to be important in the thermal decomposition of methyl cyclo-
butane, but with no evidence for surface catalysis [9].

In the present study, we believe also that the only process of significance
occurring at the wall is energy transfer. This allows an estimate to be made
of the amounts of energy transferred on average per collision.

The flat exponential model (model A) produces the best agreement with our
experimental data over the entire temperature range studied. This contrasts
with a previous conclusion [1] from VEM studies with cyclopropane that flat
gaussian, or a linear exponential, gave the best fit; however, the change in
model, if real, is in line with the somewhat decreased stepsize measured in the
present study (e.g., $<\Delta E'> \simeq 2000$ cm^{-1} $\underline{vs}$ $<\Delta E'> \simeq 2990$ cm^{-1} for cyclopropane, at
950K, both with a gaussian model). The uncertainties are such that it is prob-
ably not possible to decide definitively what the exact form of the correct model
is, and at the lowest temperatures the distinction between the models is small.

Average amounts of energy transferred per deactivating collision ($<\Delta E'>$)
do not change dramatically between the two models as can be seen from Fig. 3.
The actual values of $<\Delta E'>$ are dependent on the absolute values of $\bar{P}_c(m)$ and are
subject to some experimental uncertainty.

Plotted in Fig. 4, as a function of energy, are the ratios of the transient
population numbers of molecules, $N(E)$, in energy state E, to the numbers,

$N(E)_{eq.}$, that would be present if the molecules were in thermal equilibrium with the reactor surface with no reaction occurring. The ratios are shown after various numbers of collisions with the surface. It can be seen that at the lowest temperature, progression to the steady state occurs much more rapidly than at the highest temperature. The marked depletion of molecules at energies above the critical energy for reaction is the consequence of the chemical reaction. The curves in Fig. 4 were calculated for the exponential model; however, the qualitative picture is the same using the gaussian model.

Incubation times, in units of number of collisions, are defined as the difference, $\tau_{inc} = \bar{t}_{fp} - \bar{t}_{fp}^{ss}$, between the mean first passage time and the steady state mean first passage time; τ_{inc} is 9.4 and 7.4 at 748K, and 18.3 and 16.1 at 1123K, calculated on the exponential and gaussian models, respectively. For cyclopropane [1], incubation times were found to be a little smaller.

Plots of the probability of reaction after the nth wall collision for models A and B are shown in Fig. 5. At low values of n , the exponential model gives higher reaction probabilities per collision than the gaussian model, but this is reversed at higher values of n . Reactors with small values of m , of course, weight the small collision numbers more highly than large, and it can thus be seen why the exponential model requires the smaller value of $<\Delta E'>$ to fit the data for m = 2.6; but this method of fit then produces a higher mean probability of reaction per collision in reactors with m = 8.47 and 27.2, on the basis of the gaussian model, than is found for the exponential model.

There appears to have been no previous studies for which weak collider calculations have been made for cyclobutane. Values of $<\Delta E>$ have not been reported. Estimated values for the collisional efficiency β of various gases for energy transfer for gas-gas collisions relative to cyclobutane, have been reported around 722K, as based on the shifts in k/k_∞ curves on addition of inert gases [4]. The values of β are approximately the same as those found for cyclopropane [10] using the same procedure.

In thermal studies it is well established that complex (large) bath
molecules and, of course, the parent substrate tend to behave as strong
colliders at low temperature [11]. Recent chemical activation work at 300K,
with cyclobutane as the bath gas, has tended to favor high values of $<\Delta E>$
($= 10$ kcal mole^{-1}) for the collisional deactivation of highly vibrationally
excited methylcyclobutane [12].

The important conclusion reached by this, and by the previous study on
cyclopropane [1], is that the surface behaves as an increasingly strong colli-
der as the surface temperature is decreased. In general, at temperatures in
the vicinity of those used in conventional kinetic studies of collisional
efficiency, i.e., < 800K, wall collisions are more effective for energy transfer
than are gas-gas collisions.

Table I. Probabilities of reaction of cyclobutane per wall collision ($\bar{P}_c(m)$

in reactors (i), (ii), and (iii)

Reactor (i) (m = 27.2)	Temp(K)	1080	1034	960	890	843	790	749
	$\bar{P}_c(m) \times 10^7$	745	331	75.4	13.8	3.53	0.506	0.0783

Reactor (ii) (m = 8.47)	Temp(K)	1075	1033	958	894	840	792
	$\bar{P}_c(m) \times 10^7$	283	148	31.4	6.57	1.37	0.206

Reactor (iii) (m = 2.6)	Temp(K)	1126	1072	994	907	823
	$\bar{P}_c(m) \times 10^7$	19.2	9.54	2.55	0.413	0.0514

Appendix: Parameters used in RRKM calculation for the decomposition of cyclobutane to ethylene.

Cyclobutane frequencies (cm^{-1}) [13]:   2987, 2975, 2952(2), 2895, 2893, 2887(2), 1447(2), 1443(2), 1260, 1257(3), 1223(2), 1222, 1219, 1001(2), 926, 898(2), 7492(2), 741, 627, 197.
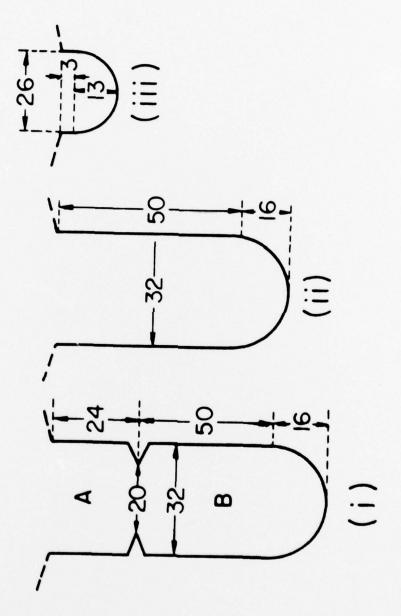
Transition state frequencies (cm^{-1}): 2980(8), 1447(2), 1443(2), 1260(2), 1250(2), 1100(2), 1000, 898, 850, 740(2), 600(2), 380, 350(2), 150
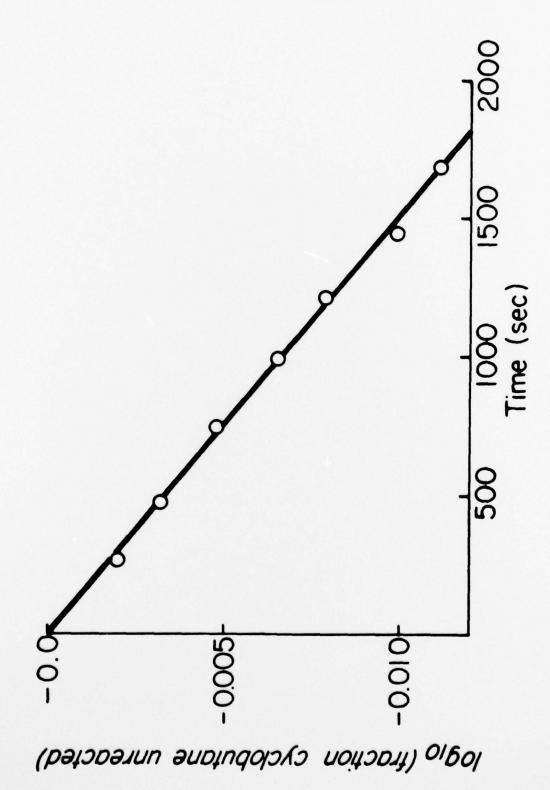
Reaction path degeneracy = 4.

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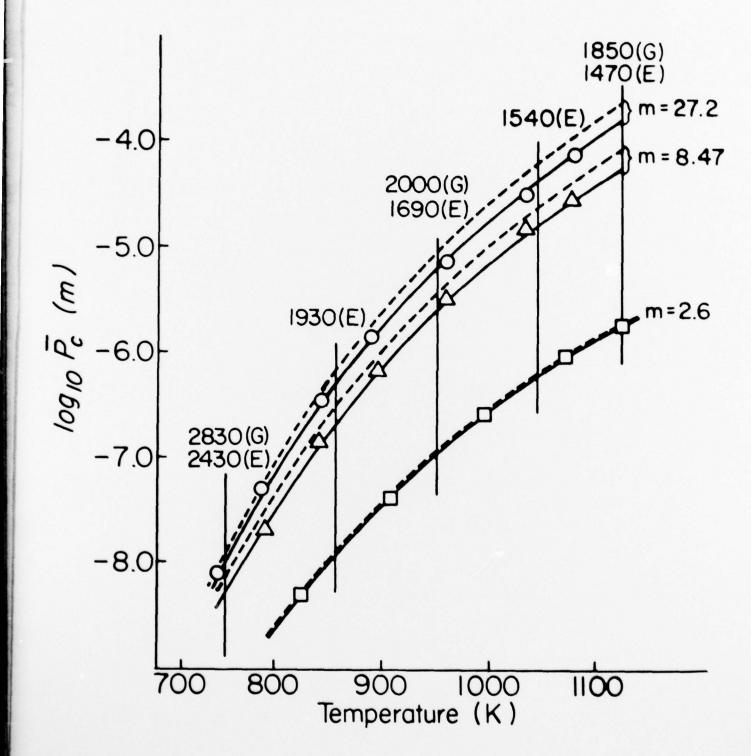   Printing Office, Washington, D.C. 20402).

Figure Captions

Fig. 1   Detail of tubular reactor fingers attached to 2 ℓ fused quartz
flask. (all dimensions are in mm)

Fig. 2   First order plot for the decomposition of cyclobutane to ethylene
at 994K for the m = 2.6 reactor.

Fig. 3   Plots of experimental values of $\log_{10} \bar{P}_c(m)$ vs temperature, and of
calculated curves for models A and B for each reactor.   Experimental
data (each point is the result of at least 6 separate runs):
$\bigcirc$, m = 27.2; $\triangle$, m = 8.47; $\square$, m = 2.6.   Solid curves are the
calculated curves using model A (exponential) and the dashed curves
are those for model B (gaussian).   Values of $<\Delta E'>$ used are indicated
at various tempepratures.   The parenthetic E and G designate the expon-
ential and gaussian models, respectively.

Fig. 4   Ratio of population of molecules relative to the equilibrium population
(at the temperature of the reactor wall) as a function of energy,
using model A.   The number of previous collisions experienced by the
molecules is shown alongside the curves;   (a)   reactor wall = 748K,
$<\Delta E'> = 2430$ cm^{-1};   (b)   reactor wall = 1123K, $<\Delta E'> = 1470$ cm^{-1}.

Fig. 5   Histogram of probabilities of reaction after collision n , and before
the next collision, as a function of n for model A (solid) curve and
model B (dashed) curve;   (a)   748K; model A $<\Delta E'> = 2430$ cm^{-1}; model B
$<\Delta E'> = 2830$ cm^{-1} (b)   1123K; model A $<\Delta E'> = 1470$ cm^{-1},
model B $<\Delta E'> = 1850$ cm^{-1}

Fig.1 Thomas Tee

Fig 2. Flowers Fri

Fig 3 Flowersilel

a   b

Equilibrium   Equilibrium

E_o E

30   20   15   10   5   0

$N(E)/N(E)_{eq}$

1.5   1.0   0.5

$E \ (10^3 \ cm^{-1})$

Fig 4 Thomas et al